

Characterization Methodology for Anode Starvation in HT-PEM Fuel Cells

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Abstract

Degradation caused by fuel starvation may be an important reason for limited fuel cell lifetimes. In this work, we present an analytical characterization of the high temperature polymer exchange membrane fuel cell (HT-PEM FC) behavior under cycled anode starvation and subsequent regeneration conditions to investigate the impact of degradation due to H₂ starvation. Two membrane electrode assemblies (MEAs) with an active area of 21 cm² were operated of up to 550 minutes, which included up to 14 starvation / regeneration cycles. Overall cell voltage as well as current density distribution (S⁺⁺ unit) were measured simultaneously each minute during FC operation. The cyclicity of experiments was used to check the long term durability of the HT-PEM FC. After FC operation, micro-computed tomography (μ-CT) was applied to evaluate the influence of starvation on anode and cathode catalyst layer thicknesses.

During starvation, cell voltage and current density distribution over the active area of the MEA significantly differed from nominal conditions. A significant drop in cell voltage from 0.6 to 0.1 V occurred after approx. 20 minutes for the first starvation step, and after 10 minutes for all subsequent starvation steps. By contrast, the voltage response is immediately stable at 0.6 V during every regeneration step. During each starvation, the local current density reached up to 0.3 A·point⁻¹ at the area near the gas inlet (9 cm²) while near the outlet it drops to 0.01 A·point⁻¹. The deviation from a balanced current density distribution occurred after 10 minutes for the first starvation step, and after ca. 2 minutes for the subsequent starvation steps. Hence, compared to the voltage drop, the deviation from a balanced current density distribution always starts earlier. This indicates that the local current density distribution is more sensitive to local changes in the MEA than overall cell voltage drop. This finding may help to prevent undesirable influences of the starvation process.

The μ-CT images showed that H₂ starvation lead to thickness decrease of ca. 20-30 % in both anode and cathode catalyst layers compared to a fresh MEA. Despite of the 14 starvation steps and the thinning of the catalyst layers the MEA presents stable cell voltage during regeneration.

Key words:

HT-PEM FC, hydrogen starvation; regeneration; voltage; current density distribution; μ-CT.

Nomenclature

P_{ac} – current density of an active point sufficiently supplied with H_2 (when current density $> 0.04 \text{ A}\cdot\text{point}^{-1}$), determined from S^{++} unit (Simulation Services®), $\text{A}\cdot\text{point}^{-1}$

i – operating current density, $\text{A}\cdot\text{cm}^{-2}$

I – operating current, A

n – number of electrons transferred per mole of reactant consumed

F – Faraday constant, $\text{s}\cdot\text{A}\cdot\text{mol}^{-1}$

\dot{m} – the rate of mass transfer by diffusion of reactants to the catalyst layer, $\text{mol}\cdot\text{s}^{-1}$

A_{ac} – sufficiently active area, cm^2

I_l – local current density, determined from S^{++} unit, $\text{A}\cdot\text{point}^{-1}$

ΣI_l – sum of local current densities, determined from S^{++} unit, $\text{A}\cdot\text{point}^{-1}$

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44 1. Introduction

45 High temperature polymer exchange membrane fuel cells (HT-PEM FC) have
46 entered the market in the last decade [1]. This type of FC is considered as a clean
47 and efficient power source for portable and stationary applications such as combined
48 heat and power (CHP) application, stand-alone power, backup power and
49 uninterrupted power supply (UPS) [2-6]. In HT-PEM FC a polybenzimidazole (PBI)
50 membrane doped with phosphoric acid is used. The typical operating temperature of
51 HT-PEM is around 160-180 °C that results in improved electrochemical kinetics for
52 electrode reaction in comparison to the low temperature (LT) PEM FC. Other
53 advantages of HT-PEM related to the enhanced operating temperature are higher
54 tolerance to impurities like carbon monoxide [7, 8] and simpler water management
55 [1]. Zhang et al. [9] investigated the dependence of the FC performance on
56 temperature. They found that in the range of 120-180 °C, the enhanced temperature
57 decreases the membrane resistance leading to higher cell power density [10].

58 However, for this type of FC there are some challenges which need to be solved, for
59 example increased degradation rate at more demanding operating temperature [11-
60 13]. Possible stressors for the operation of a HT-PEM FC are mass transfer limitation
61 due to the presence of phosphoric acid in the catalyst layer [14, 15], electrochemical
62 cycling, the start/stop procedure, and fuel starvation [16].

63 Fuel starvation, which refers to hydrogen undersupply (H_2 starvation), occurs during
64 startup and shutdown due to the rapid load variation or as a consequence of
65 inhomogeneous H_2 distribution in a single cell or between assemblies of cells [17]. In
66 addition, an uneven distribution of phosphoric acid in the the HT-PEM FC [18, 19],
67 during MEA manufacturing and/or the activation process, can also flood the catalyst
68 and results in local hydrogen undersupply [20].

69 During H_2 starvation, the local depletion of H_2 leads to an inhomogeneous current
70 density distribution over the active surface area of the MEA [17], which can either

lead to active points (P_{ac}) being sufficiently supplied with H_2 or insufficiently supplied parts of surface area defined as inactive points. The non-sufficient or inactive areas may accelerate fuel cell degradation.

Previously, the behavior under H_2 starvation was investigated for LT-PEM FCs and phosphoric acid fuel cells (PAFC). For example, Zhang et al. [21] investigated air and H_2 starvation for LT-PEM FC under controlled current and voltage modifications. They observed that current density and temperature distribution were inhomogeneous across the FC depending on the location along the flow channel. Song et al. investigated an influence of anode starvation on PAFC. The experimental results show a 5 mV loss in cell voltage after H_2 starvation [22].

Zhou et. al. [17] studied the effect of H_2 starvation in HT-PEM FC on voltage and local current density measured simultaneously under different stoichiometries ($\lambda_A < 1.0$) and at different current loads. They observed that the current density under H_2 starvation is highest in the upstream (inlet) regions, decreasing along the flow channel direction and lowest in downstream (outlet) regions due to high mass transfer resistances.

The consequences of H_2 starvation are reported differently. Liang et al. [23] observed that under H_2 starvation water electrolysis and carbon corrosion take place at the anode side of the FC. Carbon corrosion may lead to the irreversible loss of the electrochemical catalyst surface area (ECSA) [24]. Those undesirable reactions could have an influence on changes inside the MEA, e.g. in thickness and / or on the morphology [25, 26]. Therefore, to increase the lifetime of HT-PEM FCs the effects of H_2 starvation need to be investigated in more detail.

In this work we present H_2 starvation / regeneration cycles up to 550 minutes for 2 identical HT-PEM FC MEAs under operation. The regeneration step allows the evaluation of (ir)reversible degradation after each starvation step. To the best of our knowledge such a repeated combination of starvation / regeneration procedures has not yet been reported. The cyclicity of experiments was used to study the long term durability of the HT-PEM FC. Both, voltage and current density mapping were measured each minute simultaneously, allowing the evaluation of changes in FCs as a function of time and the optimization of the operational strategies to prevent FC lifetime reduction.

2. Basics

A FC produces electricity at the fixed current density i ($A \cdot cm^{-2}$). When the current is applied the electrochemical reaction leads to the depletion of the reactants at the catalyst layer. Then i can be calculated using the following equation

$$i = n F \dot{m} / A_{ac} \quad (1)$$

whereas n is the number of electrons transferred per mole of reactant consumed, F is Faraday constant, $s \cdot A \cdot mol^{-1}$, \dot{m} is the rate of mass transfer by diffusion of reactants to the catalyst layer, $mol \cdot s^{-1}$ and A_{ac} is active area, cm^2 . The operating current (I) can be then calculated by:

$$I = i A_{ac}; \quad (2)$$

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117 Under H_2 starvation, A_{ac} will be reduced due to insufficient gas flow. Meanwhile,
118 under the H_2 undersupply, the reduction of A_{ac} or respectively the inhomogenous
119 current density distribution can be measured with local current densities (i_l), for
120 example if the A_{ac} is divided over 100 points of the flow field. In case of a full
121 homogeneity the current density is equal at all the 100 points and shall be higher
122 than $0.04 \text{ A}\cdot\text{point}^{-1}$. The explanation of the chosen $0.04 \text{ A}\cdot\text{point}^{-1}$ current density will
123 follow in chapter 3.

124 In order to evaluate inhomogenous current density distribution, the 100 points can be
125 divided into two categories: the active points (P_{ac}) with a current density greater than
126 or equal to $0.04 \text{ A}\cdot\text{point}^{-1}$ and the inactive points corresponding to less than 0.04
127 $\text{A}\cdot\text{point}^{-1}$. From the sum of active points (count of P_{ac}) the active area can be
128 calculated with with the assumption below:

129

130 $A_{ac} \propto \sum P_{ac} \text{ (if } P_{ac} \geq 0.04 \text{ A)}$;

131

132 The gas flow through the bipolar plate channels can be characterized by the gas
133 partial pressure gradient which is strongly determined by the flow field design. If
134 continuous gas consumption is assumed, there is a common depletion gradient of
135 reactor gas partial pressure from inlet to the outlet [27, 28] (Fig. 1a, white arrow).
136 There is almost no difference in the partial pressure of neighboring channels (e.g. 1.-
137 5., Fig. 1a, b) compared to the adjacent channels (with opposite flow directions)
138 along the flow channel (e.g. 1. and 6., Fig. 1b), which is due to the fuel consumption
139 in the cell reaction. The partial pressure difference between two channels forces H_2
140 transport through the gas diffusion layer under the rib, which leads to an
141 improvement of the local current density.

142 The decrease in H_2 partial pressure at the catalyst surface may increase anodic
143 mass transport resistance, leading to an increase in the anode overpotential [17].
144 Therefore H_2 starvation typically results in a significant drop in cell voltage.

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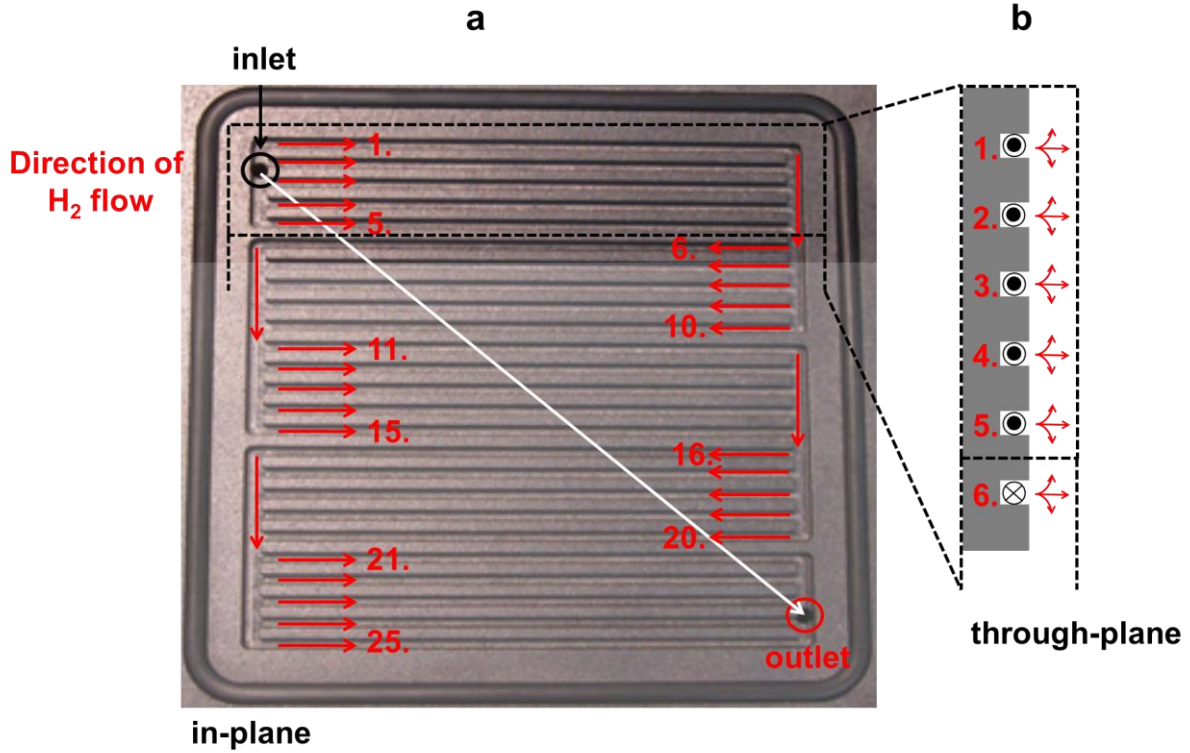


Fig. 1: a) In-plane view of serpentine flow field and **b)** schematic representation of the gas transport in serpentine flow field (through-plane view). Red arrows show the H₂ flow directions; ● indicates the gas flow perpendicular to the paper from the bottom upwards, and ⊗ indicates the flow perpendicular to the paper from the bottom downwards.

2. Experimental setup

2.1 Hardware setup

In this work, three identical MEAs Dapozol® G77 (Danish Power Systems®), were chosen for testing. This type of MEA is based on a PBI/H₃PO₄ membrane with an active area of 21 cm². The membrane was placed between two gas diffusion electrodes (GDE). The assembly with a thickness of around 0.6 mm was inserted between two graphite flow fields with five quintuple serpentine flow channels (Fig. 1a). The MEAs were tested on a FC test station FuelCon AG (Evaluator-C 70316).

A current density and temperature distribution device (S⁺⁺ Simulation Services®) was installed during the whole experiment on the anode side under the flow field (Fig. 2a). The schematic representation of the S⁺⁺ unit location under the serpentine flow field is presented in Fig. 2b (overlapped view of S⁺⁺ unit and the flow field; Fig. 1a). The S⁺⁺ unit consists of 100 points (intercepts) and each of them provides information about local current density (*I_l*), which builds up a 2D distribution map of current densities. Fig. 2b and Fig. 2c present the locations and numbering principle of 100 points from S⁺⁺ unit at the flow field.

The flow channel from inlet to outlet can be divided into 50 sections (Fig. 2d) while each section corresponds to two points at S⁺⁺ unit (e.g. i.1 and ii.1). Those 50

sections enable gas flow from one side the other (e.g. i/ii.1 - i/ii.50). However, at the intercepts i.1 / ii.1 and i. / ii.50 where MEA was fixed to the S^{++} device, there is always zero current density, therefore, those values were neglected for further calculations. The result of current density mapping will be visualized as a segmented surface, each segment consists of four adjacent points of about 0.25 cm^2 size.

Beside the 2D distribution map over the MEA, the current density was also plotted as an “unfolded” view along the flow direction from inlet to outlet, as normal in simulation work (Fig. 2e) [29]. Since each section along the flow direction corresponds to two points of the S^{++} unit, there are two current density values at each section of the unfolded view.

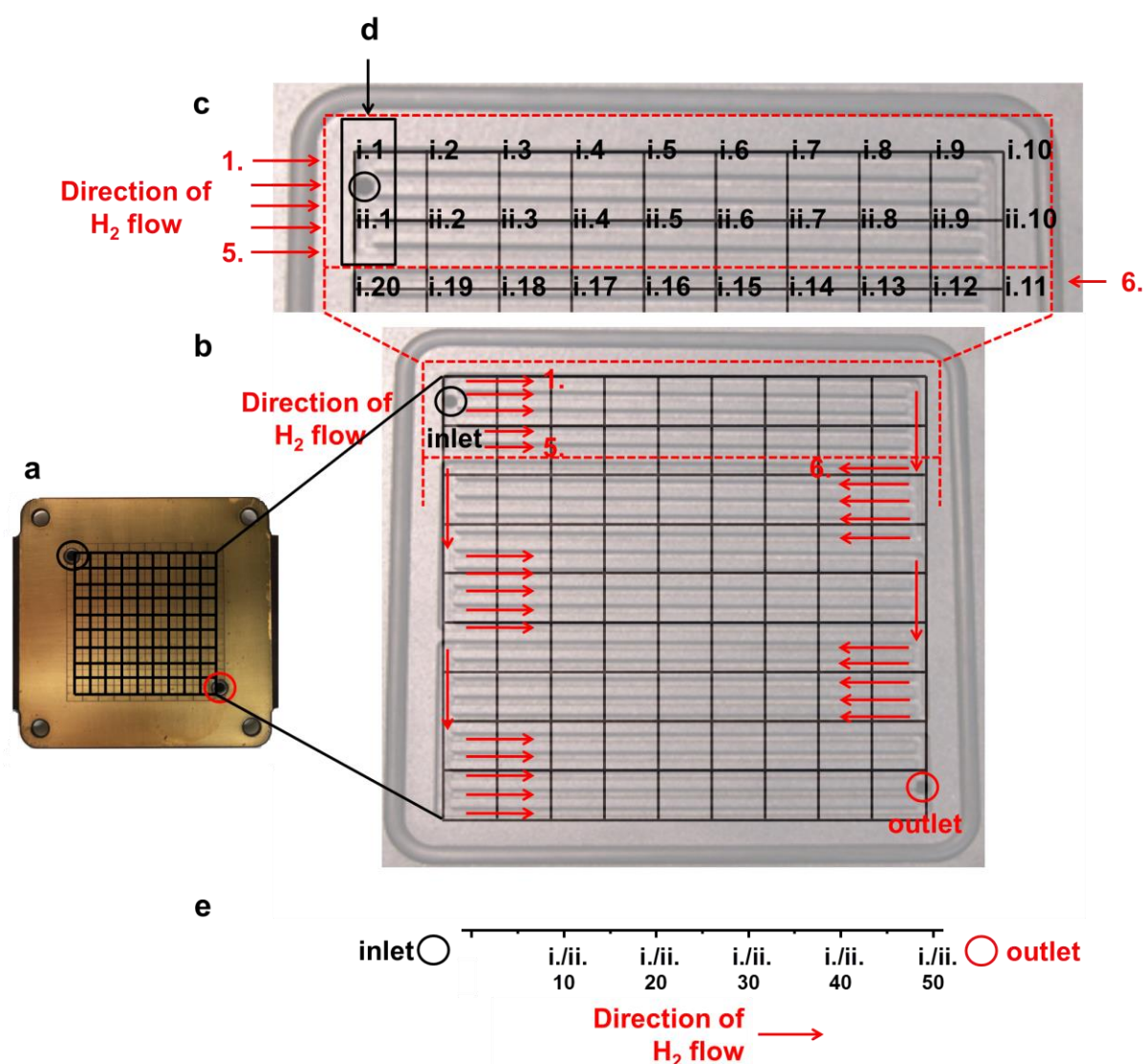


Fig. 2: **a)** Current density distribution device (S^{++} unit), **b)** serpentine flow field schematically overlapped with the S^{++} unit (location of S^{++} points (intercepts) - “folded” view, **c)** zoom into intercept locations from i.1 to i.20, **d)** exemplary section at the flow channel (points: i.1 and ii.1) and **e)** “unfolded” view of the sections (S^{++} serpentine pattern) at the flow channel (from inlet to outlet).

Micro-computed tomography (μ -CT) allows a non-destructive view into HT-PEM FC components and was conducted to measure the thicknesses of different layers of the

MEA. Measurements were carried out with the microcomputed X-ray tomography system (Skyscan 1172 Desktop-Micro-CT, Bruker, Belgium). The samples were prepared with a hole-puncher (\varnothing 4 mm). Those samples were cut from two different locations on the MEAs (1-near inlet; 2-near outlet) (Fig. 3). In order to receive comparable results the geometrical resolution of each measurement was held constant by $1.23 \mu\text{m}\cdot\text{px}^{-1}$. The thickness of defined layers, such as cathode catalyst layer and anode catalyst layer of the investigated location was measured with the help of the software Dataviewer (Fig. 3). The values for thicknesses were calculated by averaging ten values of five sagittal or coronal 2D-images [30]. The settings used for these investigations are summarized and shown in Table 1 [25].

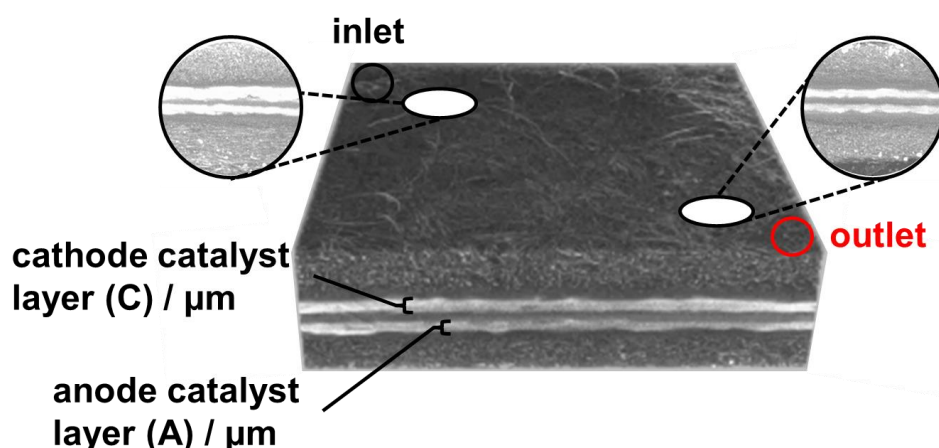


Fig. 3: Schematic presentation of an exemplary 3D μ -CT image.

Tab. 1: Operational settings in μ -CT.

Parameter	Value	Unit
Acceleration voltage	78–82	kV
Source current	96–102	μA
Sample size \varnothing	4-5	mm
Rotation step	0.2	$^{\circ}$
Random movement	10	-
Averaging	4	-
Optical resolution	1.23	$\mu\text{m}\cdot\text{px}^{-1}$
Duration	140-180	min

2.2. Experimental procedure

Prior to the electrochemical experiments the assembled HT-PEM FC was activated [31] by heating up the cell under N_2 supply to a temperature of 120°C . Subsequently reactant gases were fed: hydrogen with a stoichiometric factor of 1.5 for the anode

($\lambda_A = 1.5$) as fuel, and oxygen with a stoichiometric factor of 9.5 for the cathode ($\lambda_C = 9.5$) as oxidant while the temperature was increased to 160 °C. Shortly after, the load current was increased stepwise up to 6.35 A. The stoichiometry factor is based on the ratio between the available gas at the inlet and the required gas necessary for the reaction [32].

The intended oversupply of oxygen avoids any influences from the cathodic side of the FC and for clear separation of degradation phenomena on the anode side. The following activation procedure was conducted for each cell. From the time when stable operation was reached (0.3 A/cm² with $\lambda_A = 1.5$ and $\lambda_C = 9.5$), such condition was kept constant for 168 h in order to reach constant voltage.

Starvation / regeneration cycles were repeated for up to 550 minutes. Each cycle consisted of a starvation process with $\lambda_A = 1.0$ at 6.35 A (equals 0.3 A/cm²) and subsequent regeneration process with $\lambda_A = 1.5$ at 8.46 A (equals 0.4 A/cm²). λ_C was kept at a value of 9.5 in all conditions. The load of 6.35 A was chosen for the starvation step, representing a standard value for typical FC operation [33]. After that the FC was held under 0.4 A/cm² for 20 minutes for regeneration to assure full FC recovery after starvation.

3. Results and discussions

Previous experiments were performed under different anode stoichiometries: $\lambda_A = 0.9$, $\lambda_A = 1.0$ and $\lambda_A = 1.1$. At $\lambda_A = 0.9$ the FC immediately lost performance and the gas supply was automatically turned off due to test bench security thresholds, while at $\lambda_A = 1.1$ the FC ran stable. At $\lambda_A = 1.0$ the cell operated for several minutes, followed by a sharp voltage drop to test bench safety limits and the system was turned off. Hence, for the detailed study of starvation processes the stoichiometry $\lambda_A = 1.0$ was chosen.

As shown in Fig. 4a the starvation steps repeatedly induced a significant voltage drop. However, the immediate response during regeneration was a stable and constant voltage at 0.6 V. This could indicate that, if degradation by H₂ starvation occurred during the first starvation step it would have probably been insignificant.

In particular, the first starvation step lasted ca. 25-26 minutes for both DPS (Fig. 4b), and as expected, at $\lambda_A = 1.0$ voltage starts to drop from ca. 0.6 V after around 20 minutes down to minimal safety limits (ca. 0.1 V). Despite the voltage drop, the sum of local current densities of 100 points from the S⁺⁺ unit (ΣI_l) yielded 6.35 ± 0.30 A throughout the whole starvation step (as well as 8.46 ± 0.45 A during regeneration; Fig. 4c). The visible fluctuations in ΣI_l in Fig. 4c likely occurred due to single point current density fluctuations.

Figure 4d shows the current distribution at minutes 1 and 26 in the first starvation step for DPS-1. At minute 1 the current is well distributed all over the A_{ac}. Except for the few points directly at the inlet and outlet the current is 0.07 A·point⁻¹ (0.639 V). However, at minute 26 there is a clear deviation in current distribution, with points near the inlet reaching about 0.3 A·current⁻¹ and points near the outlet decreasing to about 0.01 A·point⁻¹. The H₂ concentration is higher near the inlet than near the outlet, which corresponds to the common gradient within the serpentine flow field (Fig. 1, white arrow) [27].

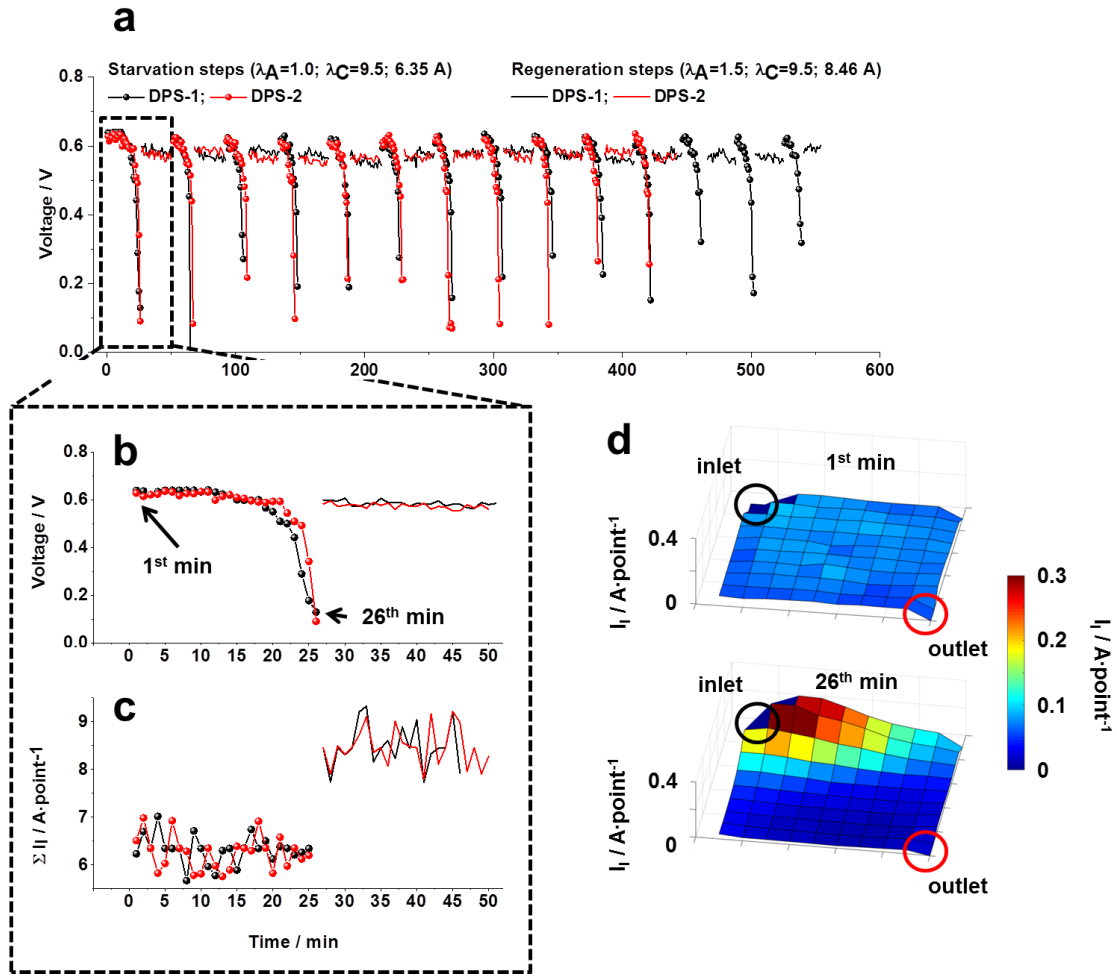


Fig. 4: **a)** Cell voltage of DPS-1 and 2 during ca. 550 min operation, **b)** zoom of voltage and **c)** sum of local current densities of 100 points from the S⁺⁺ unit for starvation / regeneration step 1 vs. time as well as **d)** 3D local current density distribution for minutes 1 and 26 in DPS-1 during starvation step 1.

For a better differentiation of the processes near the outlet the density distribution is shown as a 2D map in more detail for the lower current ranges for the minutes 1, 11 and 26 (Fig. 5a) and as current density values extracted from every point of the map in the “unfolded” view (Fig. 5b). At minute 1 the current is around 0.07 A·point⁻¹, which indicates a balanced operation and distribution over the whole area. Hence, during the first 10 minutes the system operates stable only with marginal differences in voltage and local current densities. However, at minute 11 the intercepts from i./ii.41 to i./ii.50 close to the outlet operated with a current density ≤ 0.04 A·point⁻¹ while at minute 26 more than half of A_{ac} operated below 0.04 A·point⁻¹ (Fig. 5). Next to the observed drop to 0.01 A·point⁻¹ at minute 26 the current densities near the inlet significantly increase up to 0.3 A·point⁻¹ (Fig. 4c). However, the sum of local current densities yielded the nominal current (6.35 A) such as in minutes 1 and 11.

To compensate for the two times lower current and to reach the nominal current in total (6.35 A) the remaining intercepts (80 points) increased their current densities by more than 0.07 A·point⁻¹. Therefore, the minute 11 is taken as the onset of deviation from the balanced current density distribution during starvation. The current density

of $0.04 \text{ A}\cdot\text{point}^{-1}$ indicates the instability of A_{ac} at minute 11. However, at that time the respective voltage value is still the same as in minute 1 (Fig. 4a).

The outliers (current density decrease) at the points i./ii.10 and i./ii.11 of the gas flow from inlet to outlet (Fig. 5) can be explained with the channel geometry of the flow field, since at those points the H_2 gas flow is constricted (Fig. 1a). The outlier of gas flow from inlet to outlet (e.g. intercept i.25; Fig. 5) at which current density repeatedly increased after the decrease in previous intercepts can be due to an in-plane cross-over effect passing over the geometry of flow channels [34].

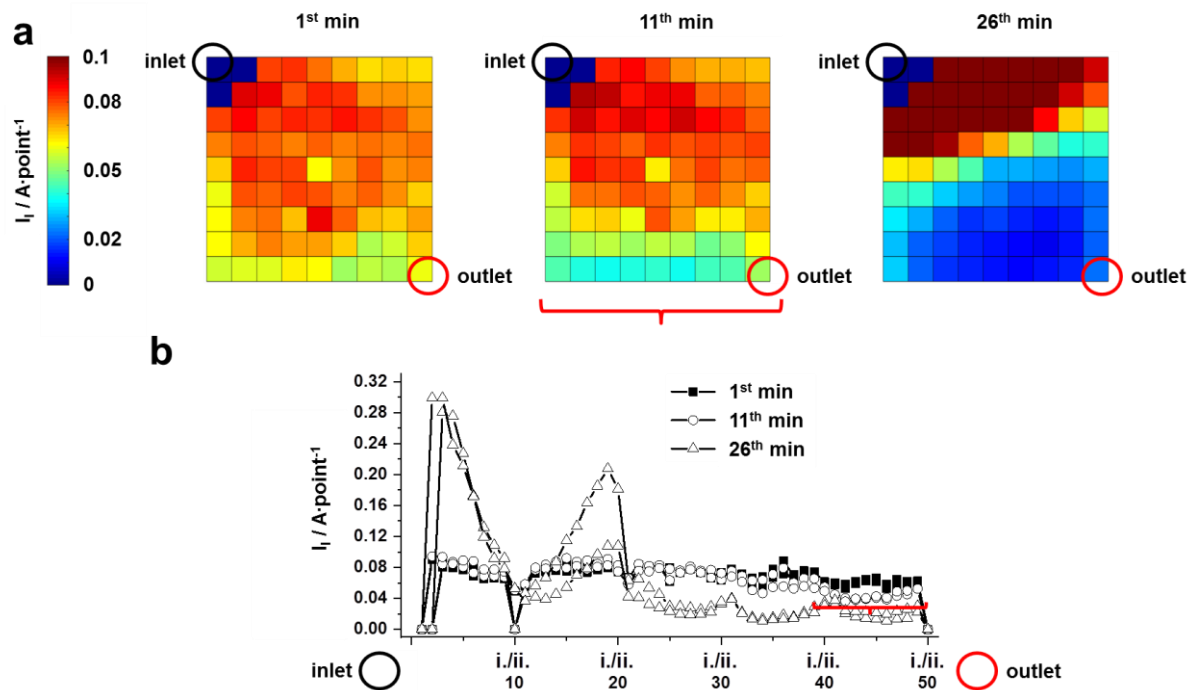


Fig. 5: a) 2D current density distribution maps during starvation step 1 at minutes 1, 11 and 26, **b)** Unfolded view of the current densities ($\text{A}\cdot\text{point}^{-1}$) for minutes 1, 11 and 26 extracted from the 2D maps (Fig. 5), red bracket points to current decrease at minute 11.

The number of points, where the local current density is $> 0.04 \text{ A}\cdot\text{point}^{-1}$ represents an area with sufficient H_2 supply (P_{ac}), which balance A_{ac} to the actual operational current. The residual points ($< 0.04 \text{ A}\cdot\text{point}^{-1}$) have insufficient H_2 supply, and the partial pressure balance of the system is disturbed. In order to balance the low H_2 partial pressure against ambient pressure, undesirable air may back-feed into the anode side of the assembly (air front) from the open outlet, which may further expand to about i./ii.20th (Fig. 4a; 5b). As soon as an H_2 and air front builds up on the anode side, the MEA acts not only as the fuel cell (hydrogen oxidation reaction (HOR) – anode side / oxygen reduction reaction (ORR) – cathode side), but also as the galvanic cell (HOR and oxygen evolution reaction (OER) –anode side / ORR – cathode side) [35].

The air - filled part of the anode side shifts the potential in the adjacent cathode electrode (ca. 1.5 V vs. reversible hydrogen electrode (RHE)). Such potential is high enough to start OER and lead to carbon oxidation currents. The electrochemical

oxidation of the carbon catalyst support (Eq. 3) is thermodynamically achievable at potential $> 0.2 \text{ V}_{\text{RHE}}$.



The consequence of the carbon oxidation of the carbon electrodes is cathode thinning i.e. loss of void volume within the cathode catalyst layer and a concomitant decrease in cathode layer thickness as reported in [36].

The anode catalyst layer may also suffer from air fronts on the anode side. Engl et al. [37] reported carbon corrosion in HT PEM FC along with a loss of a Pt electrochemical surface area (ECSA). The authors attributed this to the difference of the anode potential due to change of MEA operation between fuel cell and the galvanic cell. Similar findings of anode catalyst layer local thinning were also observed by our group [38].

As a consequence, both anode and cathode sides can undergo degradation due to anode starvation.

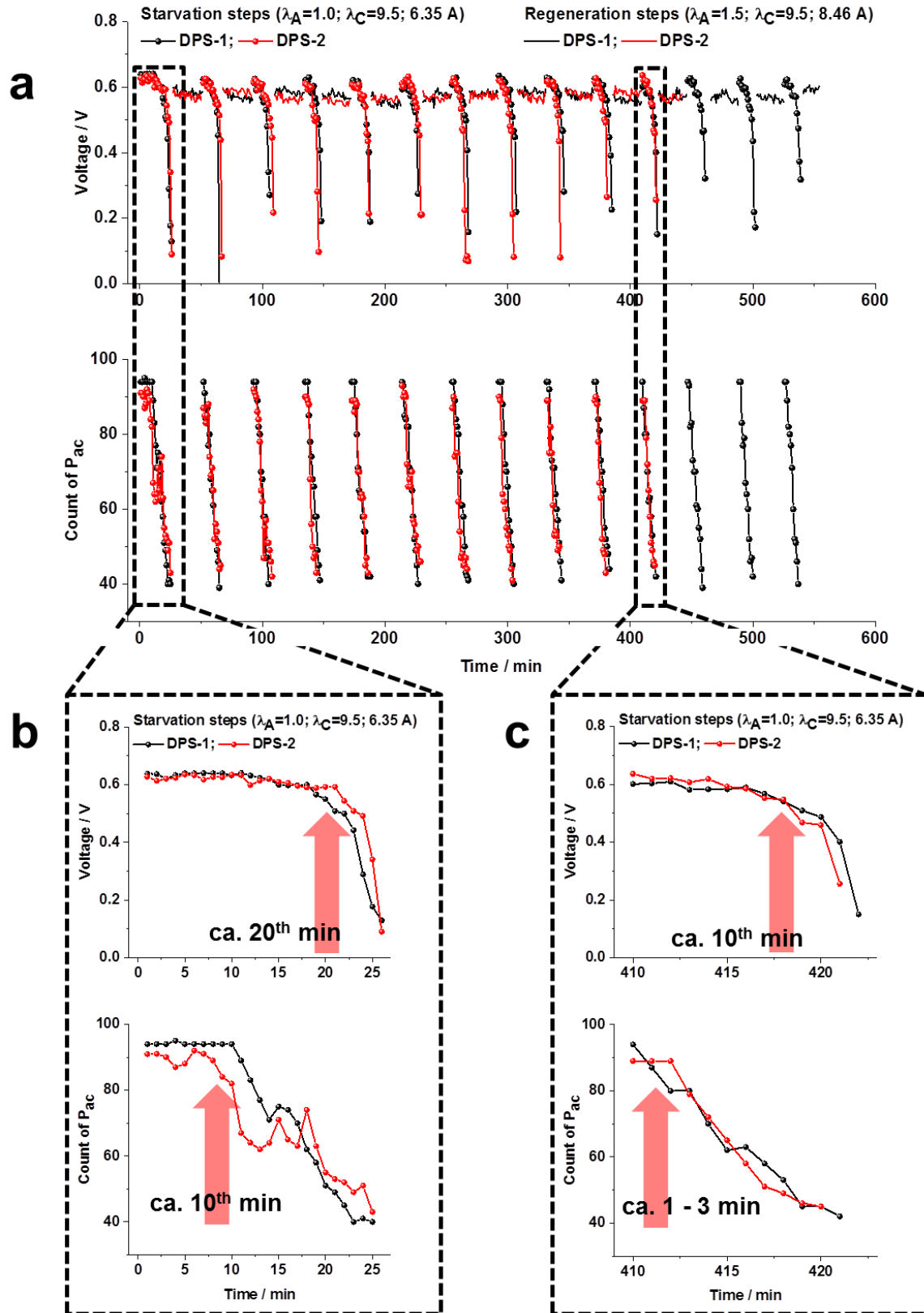


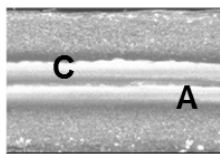
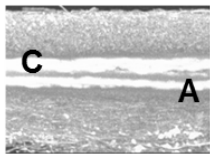
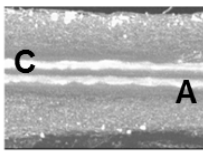
Fig. 6: a) Voltage behavior and P_{ac} for the 14 and 11 starvation steps and voltage behavior during regeneration step for DPS-1 and DPS-2 respectively, vs. time, b) zoom into the first starvation step of DPS-1 and DPS-2 and c) zoom into the 11th starvation step of DPS-1 and DPS-2.

Accordingly, the A_{ac} is divided into sufficient and insufficient H_2 supply, and $0.04 A \cdot point^{-1}$ is taken as the threshold value. The number of points with sufficient H_2 supply (P_{ac}) was determined for both DPS-1 and 2 (Fig. 6a) and, like the voltage drop, highly reproducible and essentially the same for both MEAs. Both DPS-1 and DPS-2 consist at the start of each starvation of ca. 95 sufficiently supplied points (ca. $21 cm^2$), the number of which decreases during the starvation to ca. 40 points. Hence, in the last minute of starvation the critical surface area is ca. $9 cm^2$. However, if one compares the first starvation of DPS-1 and DPS-2 and the rest of starvation steps, the time until voltage drops to below 0.2 V is in the first starvation period for both MEAs (26 min; determined by safety shut-down) about twice as long as the later starvation steps (10-15 min). The closer look at the first (Fig. 6b) and last starvation (Fig. 6c) of both DPS-1 and DPS-2 shows that the significant voltage drop starts at the first starvation step after 20 min and for the last starvation step after 10 min. Further, the decrease in P_{ac} starts after ca. 10 minutes during the first starvation step and after 1-3 minutes during the last starvation step for both DPS-1 and DPS-2. This shows that the deviation of the current distribution starts earlier than the significant drop in voltage during each starvation step. Therefore, the current distribution analysis is more sensitive to the changes occurring in MEAs and suitable for the early prediction of H_2 starvation.

The identical response in voltage and P_{ac} during H_2 starvation as well as the identical voltage response during the regeneration steps allow a first assessment of degradation effects. Since all regeneration steps showed a stable voltage at ca. 0.6 V (Fig. 6a) it can be assumed that no severe degradation took place during the starvation / regeneration steps. However, according to published experimental results possible degradation mechanisms caused by H_2 starvation may consist of (i) back-feeding processes and/or (ii) water electrolysis with subsequent corrosion processes at the anode side [37]. Those may lead to irreversible changes in MEAs, such as layer thickness and morphology [36, 39]. Therefore, in order to evaluate the impact of starvation on the catalyst layers μ -CT measurements were conducted for both anode and cathode sides, for the areas located at the inlet and the outlet. Table 2 shows the comparison of catalysts layer thicknesses obtained for the fresh MEA from the same batch (DPS-0, not been assembled in the FC test station) with those of DPS-1.

As shown in Table 2 the thicknesses of both cathode and anode catalyst layers were reduced by about 30 % (8-11 μm) compared to a fresh MEA. Apparently, H_2 starvation has a thinning effect on the layers of DPS-1. The anode catalyst layer thickness is slightly lower than the cathode catalyst layer at both inlet and outlet after H_2 starvation. However, there is almost no thickness difference between inlet and outlet of the same catalyst layers. This could be due to the fact that the total time under starvation conditions (about 550 min) was too short to have significant influence on the thickness of catalyst layer at two different places of the MEA surface. It can be concluded that after the 14 starvation steps the overall thickness of the anode and cathode catalyst layers are only slightly affected. Even if the layer thickness appears to be reduced (Table 2) the performance of the DPS remained unchanged (Figs. 4-6). Results on starvation / regeneration experiments extending the number of cycles to further days of measurement (DPS-2) will be published soon in a separate paper.

Tab. 2: Catalyst layer thicknesses as well as μ -CT images showing through-plane morphology of a fresh MEA (DPS-0) and the MEA of DPS-1 after operation. Mean values of layer thicknesses are calculated from 10 data points with single standard deviation.

Sample	DPS-0	DPS-1	
Sample status	Fresh MEA	Starvation / Regeneration	
Measurement duration / min	0	ca. 550	ca. 550
Location		inlet	outlet
μ -CT image			
cathode catalyst layer thickness (C) / μ m	35.3 ± 4.0	27.2 ± 6.2	28.6 ± 5.6
anode catalyst layer thickness (A) / μ m	35.6 ± 6.0	24.5 ± 4.0	24.3 ± 4.5

4. Conclusions

In this work, two identical MEAs from a DPS of a HT-PEM FC were cycled under anode starvation / regeneration conditions for up to 550 min, which included up to 14 starvation steps. The results show that during starvation, cell voltage and current density distribution over the active area of the MEAs significantly differed from nominal conditions. The significant drop in cell voltage from 0.6 to 0.1 V occurred after ca. 20 minutes for the first starvation step, and after 10 minutes for all subsequent starvation steps. Compared to that the voltage response of both MEAs is immediate, stable and constant at 0.6 V during all subsequent regeneration steps.

Further, during each starvation, the local current density reached up to $0.3 \text{ A} \cdot \text{point}^{-1}$ at the area near the gas inlet (9 cm^2) while near the outlet it drops to $0.01 \text{ A} \cdot \text{point}^{-1}$. The deviation from a balanced current density distribution occurred after 10 minutes for the first starvation step, and after ca. 2 minutes for the subsequent starvation steps. Hence, compared to the voltage drop the deviation from a balanced current density distribution always starts earlier. This indicates that the local current density distribution is more sensitive to local changes in the MEA than the cell voltage drop, which is an averaged measurement. Such conclusion is applicable for various types of MEAs with different active areas. This finding may help to prevent undesirable influences of the starvation process.

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5. References

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